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THE REACTION OF OXYGEN-NITROGEN MIXTURES
WITH GRANULAR ACTIVATED CARBONS BELOW
THE SPONTANEOUS IGNITION TEMPERATURE

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THE SPONTANEOUS IGNITION TEMPERATURE

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WITH GRANULAR ACTIVATED CARBONS BELOW
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1. INTRODUCTION

The presence of oxygen in the carbon network of gas adsorbent charcoals presents a research problem of long standing (1). Four pertinent topics now concerned with the oxygen-charcoal reactions are: (a) activation of the adsorbent charcoals (manufacture), (b) regeneration processes (applications), (c) the spontaneous ignition temperature (safety considerations), and (d) the use of charcoals as catalyst carriers and impregnation supports.

In an early investigation (2) it was found possible in a closed loop reactor to obtain an oxygen balance in the range 100-200°C after the charcoal had been swept with helium at 400°C. The products (H_2O , CO and CO_2) were determined in the flow gases at temperatures below 400° and, subsequently, during desorption at 200°C and 400°C. One conclusion drawn from this early study was that a steady state oxygen balance could be obtained with residual oxygen present in the products. Furthermore, the limiting oxygen chemisorption corresponded to less than 1% in surface coverage of a coconut shell charcoal.

In contrast to the above sparse oxygen coverage, later measurements (3) with ozone and oxygen formed surface complexes containing over 50 wt % oxygen at ambient temperature. At this high level of oxygen, the statistical

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surface coverage approached 100%, and the surface area (nitrogen adsorption) decreased to a very small value indicating drastic changes in available adsorption sites for nitrogen.

It is desirable to have a deeper knowledge of the initial surface composition of a charcoal that is to be used in a specific process. Thermal desorption behavior can supply such information, when conducted with samples not subjected to preliminary outgassing, heating or specified burn-offs. The results to be reported cover three characteristic temperature-dependent phenomena: (1) an anomalous desorption in which a number of maxima occur in the concentrations of CO and CO₂; (2) the formation of a surface barrier causing a decay in the CO and CO₂ concentrations with first-order rate constants at constant temperature; and (3) the attainment of a reproducible spontaneous ignition temperature (SIT) during programmed heating at a linear rate. These observations indicate a considerable complexity in the surface structure of an activated carbon.

2. ANOMALOUS DESORPTION DURING PROGRAMMED HEATING

The sample was contained in a vertical flow tube (Figure 1) and formed a cylinder 2.54 cm diameter and 2.54 cm. high. The carrier gas free of CO and CO₂ was maintained at constant flow in the range between 3 and 5 L/min and the volume percentage of oxygen in nitrogen were 100, 20, 10, 5, 1, or 0. The heating rates were 3.0, 5.0, 6.2 or 10.9°/min. Known aliquot volumes of

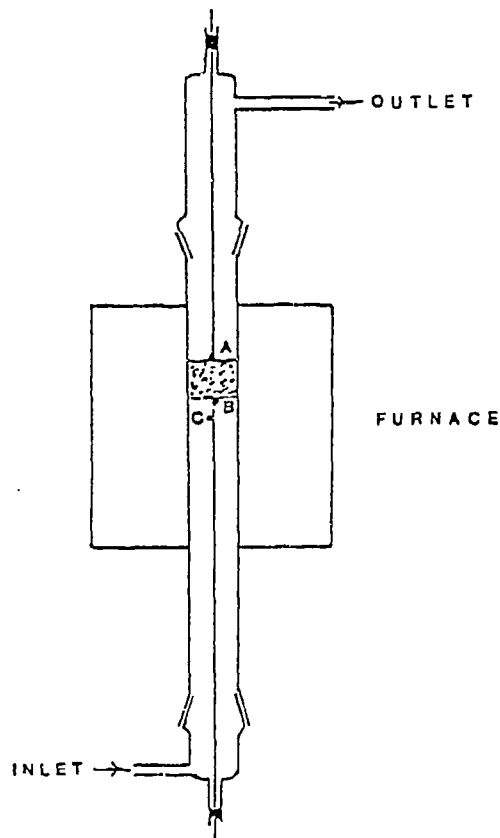


Figure 1: Experimental arrangement to determine oxidation products up to Spontaneous Ignition Temperature (SIT): A. effluent thermocouple; B. inlet temperature; C. control thermocouple.

the effluent were withdrawn for continuous analyses of CO and CO₂. The recorders were close to the main air flow and the gas samples were withdrawn with minimum mixing. The on-line response of the thermocouples A and B,

located as in Figure 1, were recorded. The thermocouple A, at the exit side responded sharply at the spontaneous ignition temperature (SIT) while the bottom thermocouple B retained its steady programmed increase.

A number of maxima were observed in the rates of emission of CO_2 and CO during the linear temperature increase in the range 50 to 200°C. The maxima in the concentration of CO_2 were about a decade above those for CO. Usually, six maxima in the rates were found as shown in Figure 2 as a function of time. The sample in this case was a coconut shell charcoal and the inlet gas flow was air purified of CO_2 and CO. The maxima were considerably reduced or eliminated upon a second heating of the same sample, Figure 3, but these could be restored after a long exposure (1 week) to the atmosphere. The maxima in the rates of emission may resemble a thermal cracking pattern of a fully developed chemisorbed oxygen complex, a model of which will be discussed below.

The pattern of anomalous desorption was approximately the same for the first heating in 100% nitrogen. As shown in Figure 4 the maxima in concentration of CO_2 are well defined, but are displaced towards higher temperatures. The oxygen in the CO and CO_2 had to come from the surface composition of the charcoal and could not be replaced as in the case of nitrogen-oxygen mixtures. The residual surface complex resulting from a heating in nitrogen contained less oxygen and had a greater thermal stability.

The simultaneous recording of the temperature of the exit gases (thermocouple at the top center of the charcoal bed) indicated a pattern in temperature-gradient decreases, see Figure 5, that corresponded to the positions of maxima in CO and CO_2 desorption. The decreases are compatible

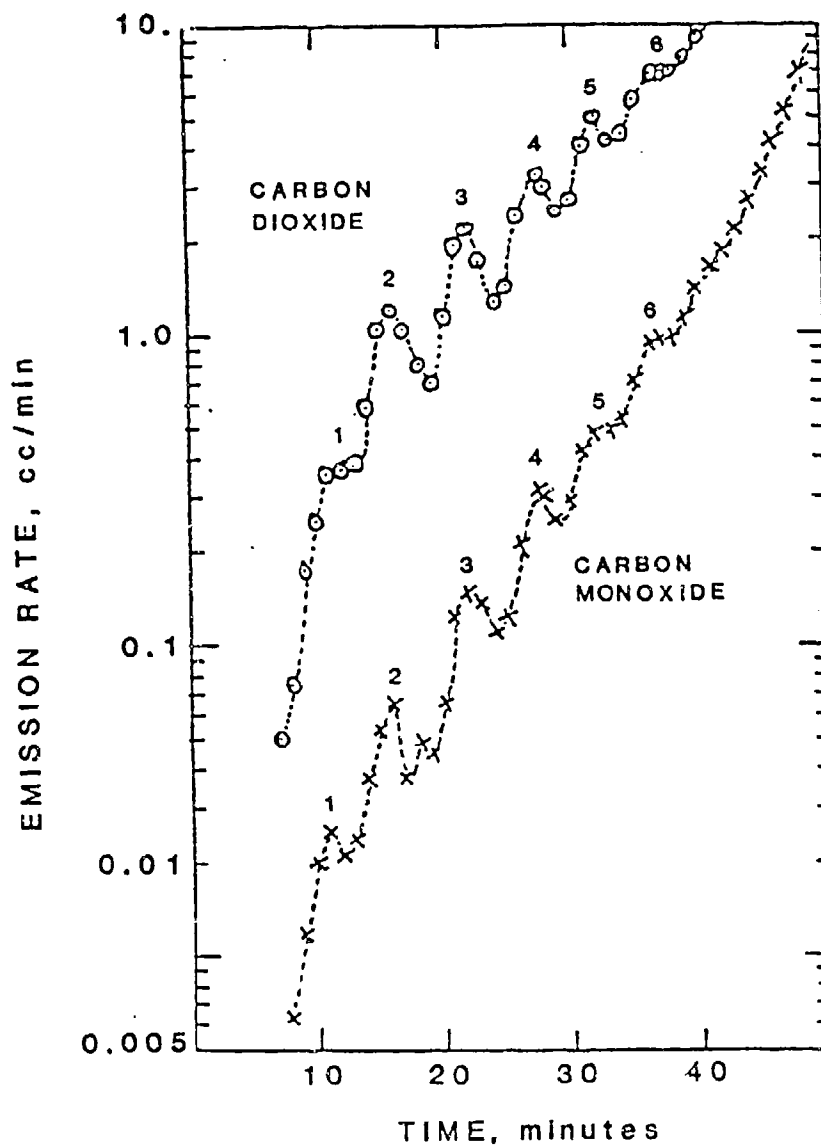


Fig. 2: Anomalous desorption of CO and CO₂ in programmed heating (5°/minute) and an air flow of 5L/minute (coconut charcoal G-210). The position for SIT does not appear in the designated time period.

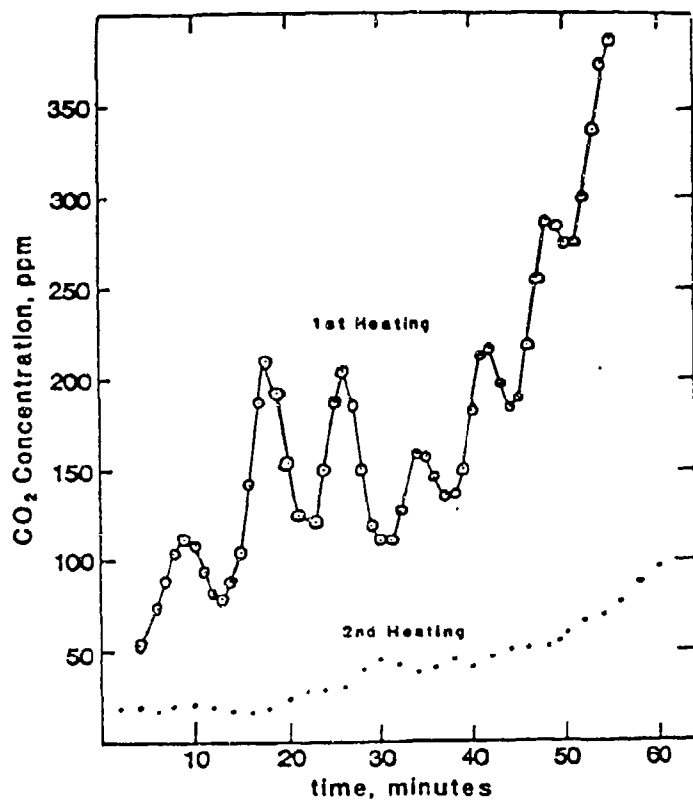


Fig. 3:
Anomalous desorption of CO₂.
Top curve for 1st Heating;
lower curve for 2nd Heating.

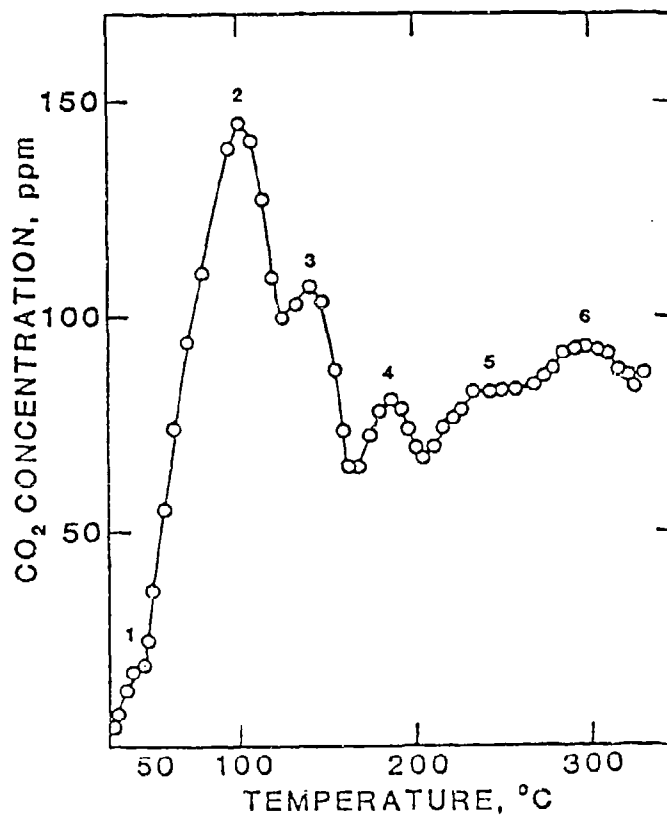


Fig. 4:
First heating (5.3°/minute)
of coconut charcoal (G-210)
in 100% nitrogen; CO₂ ppm
vs. temp.

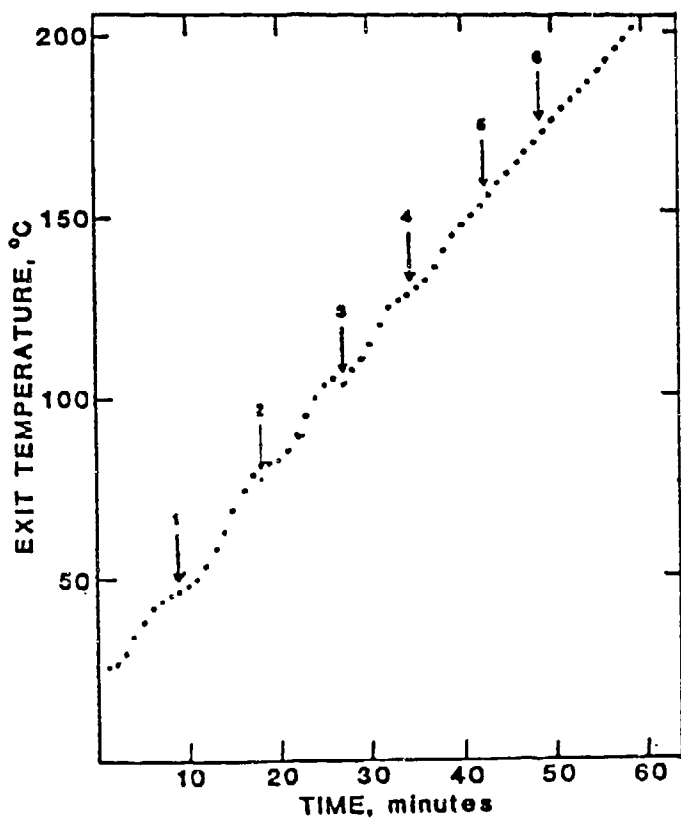


Fig. 5:
Thermometric analysis from
the programmed heating of
coconut shell charcoal
(G-210).

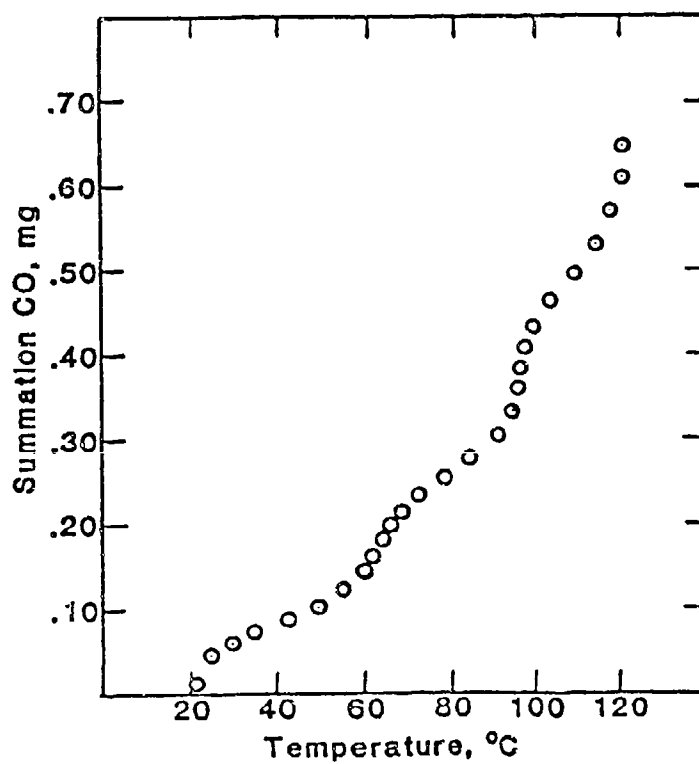


Fig. 6:
Integrated desorption of CO
from a coconut shell char-
coal (initial weight 6.32 g)
(3290).

with endothermal surface reactions that would occur in the progressive decomposition of the oxygen complex on the surface.

Thermal desorption patterns for various carbons were approximately the same at different oxygen concentrations of the carrier gas. The peak heights, however, varied with different carbons. The emission of CO was always less than that of CO₂ over the observed temperature range. A partial summary of the maxima observed is given in Table 1 which gives the times and temperatures where these occurred.

When integrated desorptions are plotted as a function of temperature, the pattern of desorption maxima is less pronounced. An example (Figure 6) is given for CO from a coconut charcoal oxidized in air over the temperature range 20 to 120°C.

Table 1: Thermal desorption maxima in the CO and CO₂ emitted from surface oxygen complexes on activated charcoals.

Peak	1	2	3	4	5	6
3290, 20% O ₂ (G-210) time, min. temp. °C	9 54	18 90	26 114	34 138	42 164	48 181
3370, 20% O ₂ (CAL) time, min. temp. °C	8 44	12 76	27 141	33 166	36 173	44 205
3407, 10% O ₂ (G-210) time, min. temp. °C	8 38	- -	26 96	33 132	40 173	46 205
3406, 5% O ₂ (G-210) time, min. temp. °C	10 38	18 51	24 93	33 140	40.5 183	46 215
3372, 100% N ₂ (G-210) time, min. temp	8 40	17 100	23 140	31 135	52 290	75 360

3. THE FORMATION OF CARBON MONOXIDE AND CARBON DIOXIDE AT CONSTANT TEMPERATURES BELOW SIT

The oxygen concentrations in the measurements made at constant temperature covered the range from 1% oxygen in nitrogen to 100% oxygen. Thus, using total flows of 5L/min, the oxygen ranged from 65 to 6400 mg/min and assured an excess of oxygen relative to that desorbed as CO or CO₂. An example of the temperature control is shown (Figure 7) for the coconut shell charcoal (G-210) in 100% oxygen in which s.d. is the standard deviation of the designated temperature control. The programmed temperature was increased stepwise as shown in Figure 7.

The results for the desorption of CO and CO₂ are shown in Fig. 8 (1% O₂ in N₂) and in Fig. 9 (100% O₂). The concentrations of either CO or CO₂ rose to an initial maximum upon changing the temperature, but soon decreased with an exponential decay of apparent first order as the constant temperature was attained. The rate constants for the decrease in CO and CO₂ concentrations are (Table 2) of the same order of magnitude and there is a trend to lower values in higher oxygen concentrations.

The apparent heats of activation for both the desorbed CO and CO₂ were calculated from plots of $\ln k$ vs. $1/T$ and were of relatively small orders of magnitude. There was a definite decrease with increase in the oxygen concentration (Table 3).

The temperature steady state of 313°C, (standard deviation 1.2°) was realized in a flow of 100% O₂ at 5L/min (Fig. 9), is of particular interest. As will be shown below, the SIT for this charcoal is 325°, and the ability to maintain temperature control in a flow of 100% oxygen indicates that an effective boundary barrier still exists at a temperature close to the SIT and this barrier prevents the excess oxygen reaching the bulk of the sample.

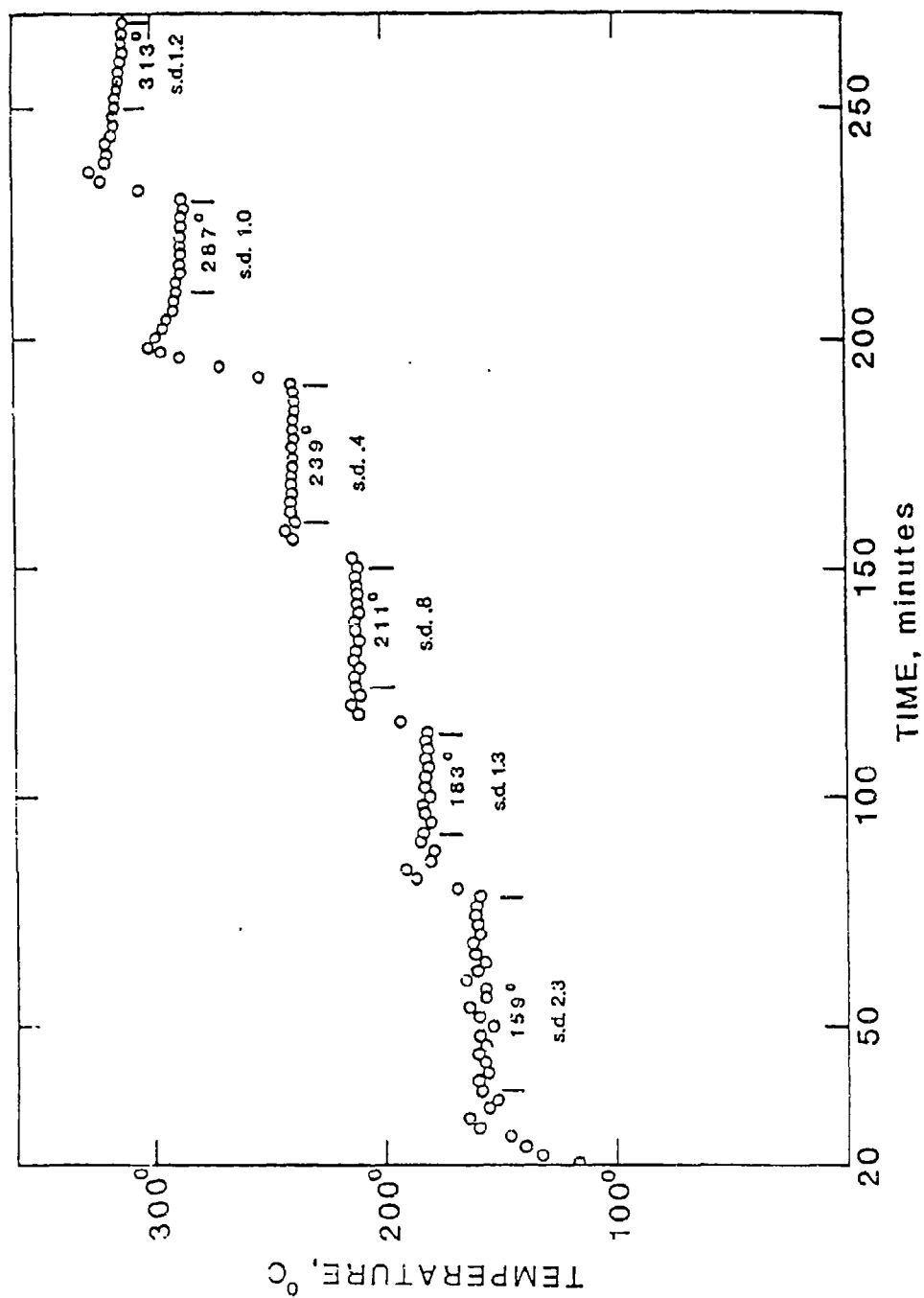


Fig. 7: Temperature control realized in the desorption measurements for a coconut charcoal (G-210) in a flow of 100% oxygen at 5L/min.

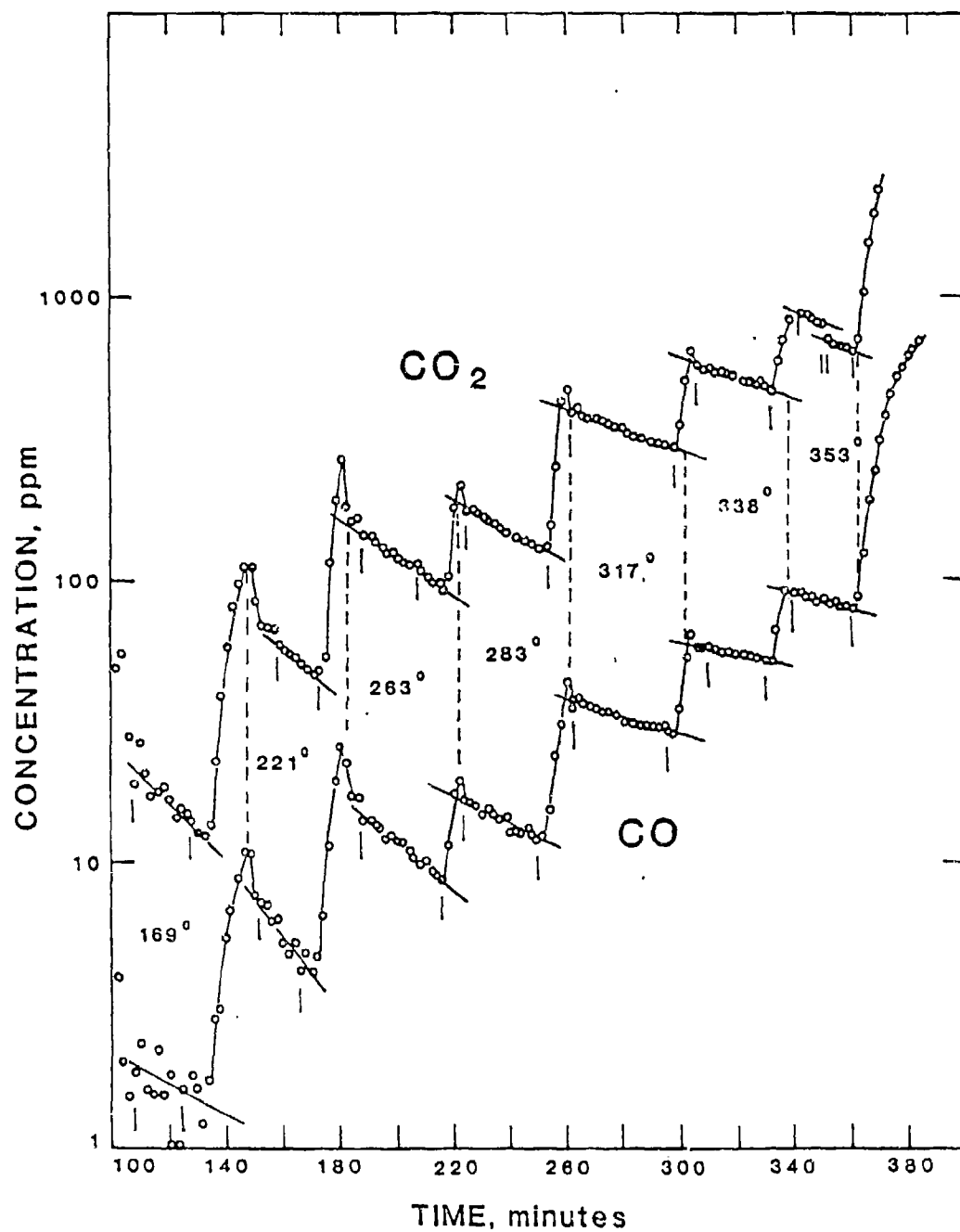


Fig. 8: Exponential decay in the concentrations of CO and CO_2 at the indicated temperature with 1% O_2 in nitrogen at a flow of 5L/minute.

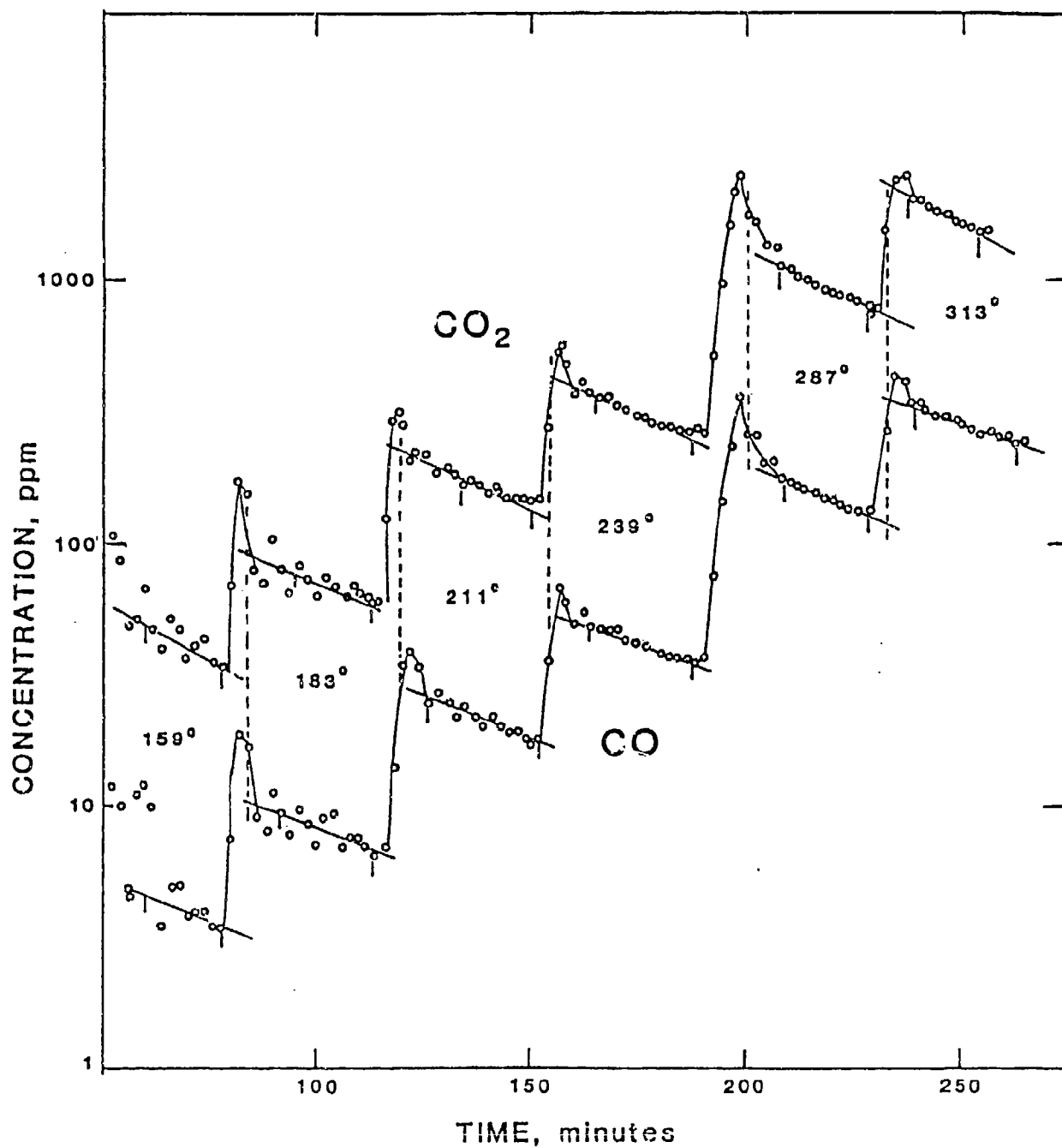


Fig. 9: Exponential decay in the concentrations of CO and CO₂ at the indicated temperatures in 100% oxygen at a flow of 5L/min.

Table 2: Rate constants for the decrease in CO and CO₂ concentrations at constant temperature for coconut charcoal.

% O ₂	°C	k _{CO}	k _{CO₂}
1%	169	.043	.0230
	221	.0324	.0169
	263	.0184	.0158
	283	.0120	.0141
	317	.007	.0087
	338	.0046	.0065
	353	.0065	.0090
20%	146	.0326	-
	188	.0280	.0258
	226	.0251	.00258
	250	.0222	.0180
	291	.0173	.0194
	278	.0180	.0123
	318	.0140	.0143
100%	159	.013	.013
	183	.012	.014
	211	.0125	.012
	239	.0122	.0099
	287	.0128	.014
	313	.0120	.0096

It appears that the desorption of CO or CO₂ is independent of the gas phase concentrations of these products. In one experiment (3316) the inlet composition was 20% oxygen plus 1120 ppm CO₂; the CO produced was the same as with 20% oxygen alone. Also, in a second experiment (3317), the inlet composition was 20% oxygen plus 1140 ppm CO; the CO₂ produced was the same as with 20% oxygen alone. The decay constants for CO₂ in the latter experiment were plotted (Figure 10) with $\ln k$ as a function of $1/T$. The activation energy was 5.2 kcal. Similarly, with excess CO₂, the activation energy for the desorption of CO (3316) was 6.1 kcal.

Table 3: Apparent heat of activation in the desorption of CO and CO₂

% O ₂	$\Delta t^{\circ}\text{C}$	Heat of Activation	
		CO	CO ₂
1%	169-352	6.7	3.3
20%	146-318	2.3	2.9
100%	159-313	0.1	0.7

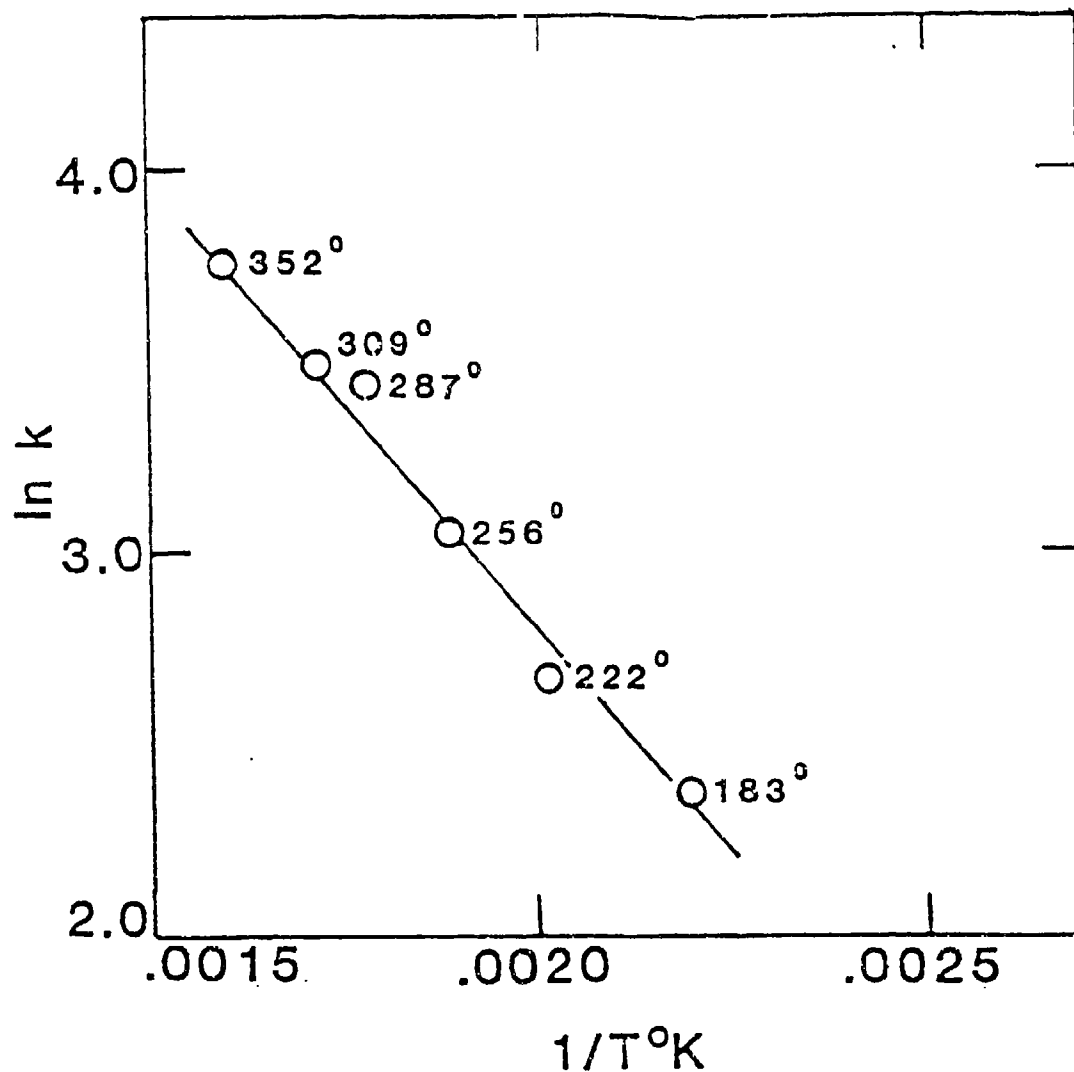


Fig. 10: Arrhenius plot for the decay of CO₂ concentration in excess CO (1144 ppm plus air) at 5L/min (Test 3417).

4. SPONTANEOUS IGNITION TEMPERATURE (SIT)

When a charcoal bed (2.5 cm dia. and 2.5 cm high) is heated in a constant upward air flow and at a linear heating rate, an abrupt increase in the exit temperature (top center of bed) occurs when the SIT is reached. There is good reproducibility (Table 4) both among different subsamples of a given charcoal and upon repeated use of the same sample.

Table 4: Reproducibility of SIT Determinations (G-210) Coconut Charcoal)

Air Flow L/min	Heating Rate °/min	SIT °C
Different Samples		
3.2	10.9	348
3.2	5.2	339
3.2	6.2	343
6.2	5.0	349
5.0	3.0	331
	Mean	342°
	Standard Deviation	7.6°
Same Sample		
5.0	3.0	331
5.0	2.8	331
5.0	3.0	345
5.0	2.9	341
	Mean	337°
	Standard Deviation	7.1°

The SIT is almost independent of the oxygen concentration (Table 5) from 100% to about 5% oxygen in nitrogen. In this range, the oxygen is in great excess relative to that in the oxidation products. Before the SIT is reached, all charcoal particles are non-luminescent; at the SIT a large number of particles become incandescent, usually at the exit end of the charcoal bed. At 1 volume % O_2 in N_2 there is evidence that the oxidation that could take place at SIT is starved with respect to oxygen.

Table 6: Influence of Adsorbed Hydrocarbons on the SIT of GX32, Petroleum Coke Base

Adsorbate (wt. %)	SIT °C
None	420,439
1% hexane	440
9% octane	420
10% decane	440
10% dodecane	310
10% tetradecane	290

5. DISCUSSION

The present studies on carbon-oxygen systems are in a lower temperature range than many previously investigated (1,7). Moreover, the surface composition had not been modified by outgassing, heating, or specified burn-offs. As previously reported (6), the fractions of the surface area occupied by the chemical constituents of an activated charcoal can be estimated because of the large surface area (1200-1600 m²/g). Most of the hydrogen and oxygen, no matter how distributed, must be present in or near the surface in the same mole ratio calculated from the chemical composition. In the example shown in Table 7, the initial oxygen was estimated to cover about 0.7% of the surface (nitrogen, point B) which is equivalent to 8.4 out of 1200 m²/g.

Table 7: Composition and Surface Area Fractions of Charcoal, G-210 (1200 m²/g, point B)

	Weight %	Mole fraction in solid	Area fraction %
C	94.7	.977	99.1
H	0.1	.012	0.2
O	1.4	.011	0.7

An attempt will be made to correlate the present kinetic data in terms of a surface-barrier model. Koresl and Soffer (8) have applied such a model to systems of physical adsorption on molecular sieve carbons. In the chemical reaction of oxygen with the carbon networks in activated charcoals, a surface barrier could form that would be rate controlling in the transfer of oxygen through the barrier to reactive carbon sites. Alternative models have employed intraparticle diffusion in a void system of postulated geometry as the controlling step. Such a model must be concerned with the diffusion of oxygen into the particle and of carbon dioxide, carbon monoxide, and water vapor out of the particle. However, the void geometry of a charcoal particle is not simple and, in general, not known in sufficient detail to deal with the mixed gas composition involved.

The case for a surface-barrier model rests on several observed properties of the system:

(1) There is a very large microscopic void content within a particle of an activated carbon as demonstrated by intense x-ray forward scattering (9). An activated carbon particle appears to be an elaborate system of intercommunicating voids surrounded by carbon atoms.

(2) The oxygen content in the surface of the original sample is a small fraction of the total surface as shown by the above example (Table 7) and from previous investigations (7).

(3) On the first heating CO and CO₂ are always desorbed starting at ambient temperature. The products appear to be decomposition products from the original surface complex. The CO and CO₂ evolution are drastically reduced by a subsequent heating.

(4) An enhanced reactivity with oxygen exists with the edge atoms of a basal plane array of carbon atoms relative to the greater number of carbon atoms within the network (10).

(5) Rates of desorption of the CO and CO₂ have Elovich kinetics at constant temperatures below spontaneous ignition.

(6) A small activation energy exists for the desorption of CO and CO₂ at temperatures below the SIT.

It is, therefore, suggested that a surface chemical barrier exists within what can be termed the aerodynamic boundary of each particle (11). With all oxidation experiments above 1% O₂ in nitrogen, a sufficiently high partial pressure of oxygen is present to maintain surface oxygen saturation. The oxygen content of the CO and CO₂ products is far less than that introduced (see Table 5).

The measurements in 100% oxygen and in 100% nitrogen, first heatings, deserve special mention. Although the resulting magnitudes of CO₂ and CO concentrations are different, the volume ratios, CO₂/CO, are quite similar. The trend (Figure 11) is that of a steady steep decrease from about 100 to 15 over the range 100°-150°C. At higher temperatures the ratio in 100% nitrogen is 12 and in 100% oxygen the ratio up to the SIT is almost constant, varying from 9 to 6. The volume ratio in air (Table 8) compares best with that in 100% oxygen. It is in the high ratio region that the anomalous desorption of CO₂ and CO takes place. There is little steric restriction on the possible configurations of the oxygenated fraction in the aerodynamic boundary surface and these can develop as elaborately as the chemical conditions permit. One can attribute, therefore, the anomalous desorption to discrete variations in the composition of the aerodynamic surface.

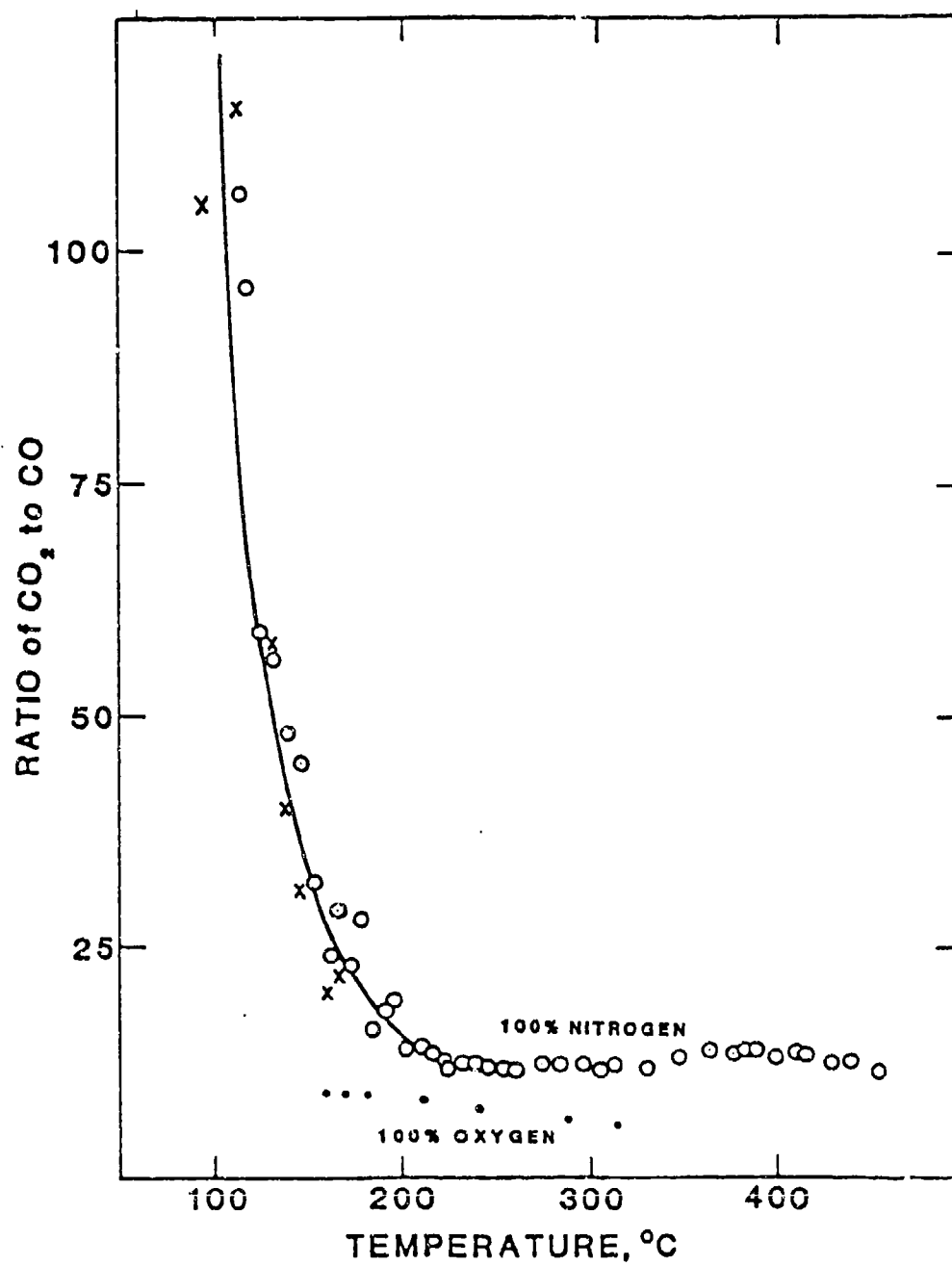


Fig. 11: Volume ratio of CO₂ to CO in the programmed heating of coconut charcoal in 100% N₂ or in 100% O₂.

Table 8: Variation in volume ratio CO_2/CO

Mean Temperature °C	2	Volume Ratio	
		Mean	S.D.
100% O ₂			
159		8.6	2.3
183		8.7	0.3
211		8.2	0.1
239		7.5	0.1
287		6.2	0.2
313		5.7	0.1
AIR			
156		5.3	1.1
188		6.7	1.0
226		8.0	0.6
250		8.2	0.3
298		7.8	0.3
324		6.9	0.2
279		6.0	0.2

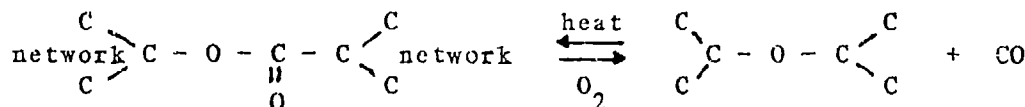
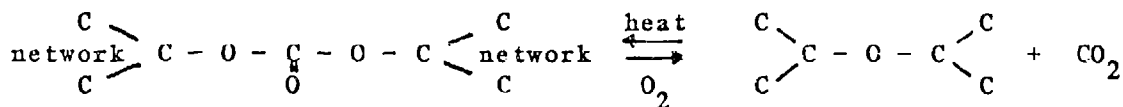
The overall behavior is then a rapid reaction of the gas phase oxygen with a chemical species in the surface barrier (11). The thermal stability of the latter will then vary with temperature, but any reactive carbon species formed rapidly combines with oxygen at a faster rate than the rates of desorption of the products. Finally, at the SIT, the rate of desorption from the surface barrier exceeds the rates of formation of the oxygen complex and gas phase oxygen can contact the carbon network below the aerodynamic boundary of the particles.

It was shown (3) that there is a continuous interconnecting porous structure in an activated charcoal that permits entrance of physically adsorbed species into the internal structure from any part of the boundary of the particle. For example, the nitrogen adsorption (77.4°K) per gram of charcoal is the same after 95% burn off in air at 400-500°C. However, such

free access may not be present for a chemisorption process. One case in point is the reaction of ozone with adsorbent charcoal (3) at ambient temperature. The oxidation complex is retained and appreciably reduces the nitrogen adsorption. The surface barrier model suggested above for the present oxidation results appears to have intermediate properties. The sudden appearance of incandescent particles at the SIT can be due to the free entry of oxygen and the rapid temperature increase due to the resultant heat of combustion.

Below the SIT a heat of activation is indicated for the processes by which CO and CO₂ leave the surface barrier (Table 3). Although the heat of activation decreased with increase in the oxygen partial pressure, the barrier remained intact and prevented ignition. The inert gas nitrogen had little influence on the reaction rates (Table 2), contrary to what is expected from a system that is diffusion controlled. The minor effects observed are attributed to variations in heat transfer and flow conditions of the experiment.

The chemical composition of the surface barrier (on a carbon) has not been established. Among possible oxygenated entities that might be postulated to exist (having a surface coverage not exceeding 1%) are a carbonate configuration and that of an acid anhydride. These groups could decompose and reform as follows:



The known thermal stability of the postulated ether linkage in the temperature range of the present studies would favor its presence among the surface products. The spacing between the ether oxygens in $\begin{array}{c} - O - C - O - \\ \quad \quad \quad O \end{array}$

(2.7A) is commensurate with that spanning the six member carbon ring (2.8A). Such a grouping, located along the edge atoms of the basal plane structure, would be available without steric interference in the aerodynamic surface zone. The rate of transport of molecular oxygen is hindered by mutual repulsion with the surface oxygen. However, the validity of applying known organic reactions for the identification and estimate of surface groups can be questioned (1). Most organic reactions known to exist in solution or in the gas phase can be appreciably modified in vacuo where the reactants and products can be adsorbed on the carbon surface.

6. CONCLUSIONS

There is strong evidence for a chemical surface barrier on activated charcoals when subjected to $O_2 - N_2$ gas mixtures flowing through the sample at temperatures below the SIT. The emission of CO and CO_2 at constant temperature was found to decrease logarithmically with time and the calculated heats of activation ($\ln k$ vs $1/T$) were of similar orders of magnitude for both products. A definite trend to somewhat lower heats of activation were determined with increase in oxygen partial pressure.

The anomalous desorption of CO and CO_2 has been observed in the temperature range where the surface barrier is well developed chemically. The anomalous desorption was not present after the sample had been either heated to the SIT, outgassed in nitrogen, or evacuated. It is present on all commercial activated carbons and could play a part when the carbon is used as a catalyst or impregnation support.

When the temperature reaches the point of spontaneous ignition, the oxygen used in the chemisorption processes can be differentiated from that used in combustion. This was shown (2) by the difference in composition observed in a sample of the steady state gas phase compared to the gas composition when the product gases are desorbed from the same sample. Once the SIT is reached, a series of run-away combustion reactions takes over.

A regenerative process is best undertaken at temperatures below the SIT in order to avoid run-away combustion. This suggests the use of repeated short cycles on-stream, combined with short cycles of regeneration, in order to maintain a charcoal of maximum efficiency.

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8. APPENDIX 1: LIST OF FIGURES

Figure 1: Experimental arrangement to determine oxidation products up to Spontaneous Ignition Temperature (SIT): A. effluent thermocouple; B. inlet thermocouple; C. control thermocouple.

Figure 2: Anomalous desorption of CO and CO₂ in programmed heating (5°/minute) and an air flow of 5L/minute (coconut charcoal, G-210).

Figure 3: Anomalous desorption of CO₂. Top curve for 1st Heating; lower curve for 2nd Heating.

Figure 4: First heating (5.3°/minute) of coconut charcoal (G-210) in 100% nitrogen: CO₂ ppm vs temperature.

Figure 5: Thermometric analysis from the programmed heating of coconut shell charcoal (G-210).

Figure 6: Integrated desorption of CO from a coconut shell charcoal (initial weight 6.32 g) (3290).

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Figure 8: Exponential decay in the concentrations of CO and CO₂ at the indicated temperature in 1% O₂ in nitrogen at a flow of 5L/min.

Figure 9: Exponential decay in the concentrations of CO and CO₂ at the indicated temperatures in 100% oxygen at a flow of 5L/min.

Figure 10: Arrhenius plot for the decay of CO₂ concentration in excess CO (1144 ppm plus air) at 5L/min (Test 3417).

Figure 11: Volume ratio of CO₂ to CO in the programmed heating of coconut charcoal in 100% N₂ or in 100% O₂.